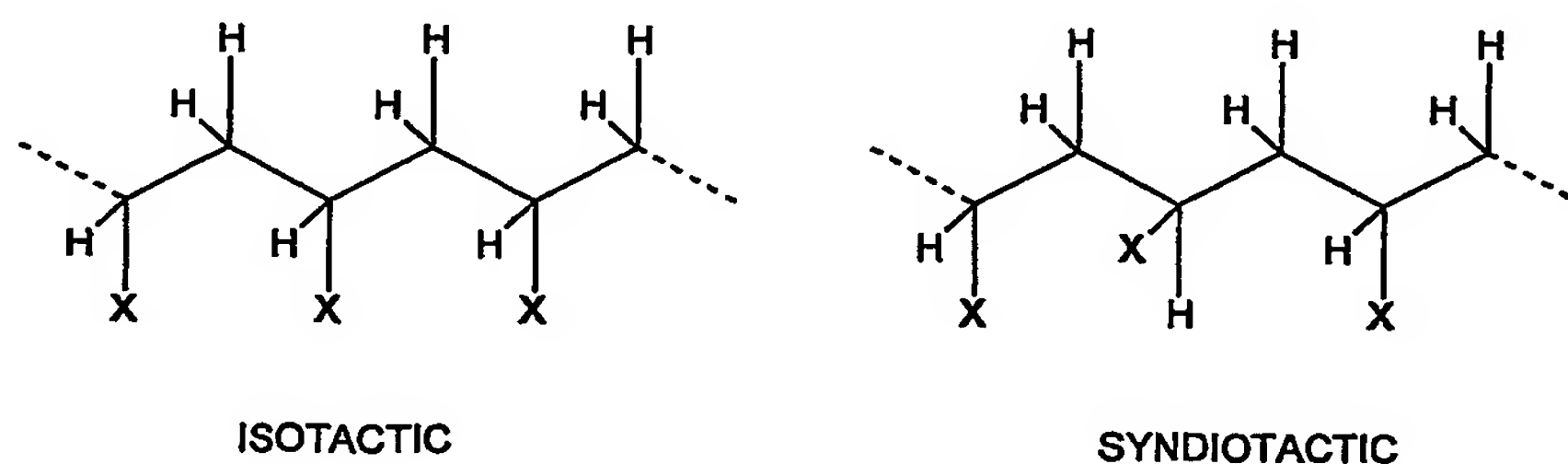


COORDINATION COMPLEX

The present invention relates to a series of discrete, well-defined coordination
5 complexes. More specifically, the invention concerns the use of Group 2 metal
complexes in the controlled polymerisation of acrylate and alkylmethacrylate
monomers.

Over recent years, an important technological objective has been the controlled, 'living'
10 polymerisation of acrylate and alkylmethacrylate monomers to give products of
controlled molecular weight and molecular weight distribution, and to provide access to
block co-polymer materials. Examples of controlled or 'living' polymerisations include
anionic polymerisation [C. Zune, R. Jérôme, Prog. Polym. Sci., 1999, 24, 631], group
transfer polymerisation [O.W. Webster, W.R. Hertler, D.Y. Sogah, W.B. Farnham,
15 T.V. Rajanbabu, J. Am. Chem. Soc., 1983, 105, 5706], atom transfer radical
polymerisation [K. Matyjaszewski, J. Xia, Chem. Rev., 2001, 101, 2921], immortal
polymerisation [T. Aida, S. Inoue, Acc. Chem. Res., 1996, 29, 39], catalytic chain
transfer polymerisation [T.P. Davis, D.M. Haddleton, S.N. Richards, J. Macromol. Sci.
Rev. Macromol. Chem. Phys., 1994, C34, 243], screened anionic polymerisation
20 [D.G.H. Ballard, R.J. Bowles, D.M. Haddleton, S.N. Richards, R. Sellens, D.L. Twose,
Macromolecules, 1992, 25, 5907] and metal-free anionic polymerisations [M.T. Reetz,
Angew. Chem., Int. Ed. Engl. 1988, 27, 994].

Stereospecific polymers can exist in two different forms, isotactic and syndiotactic, as
25 shown below.



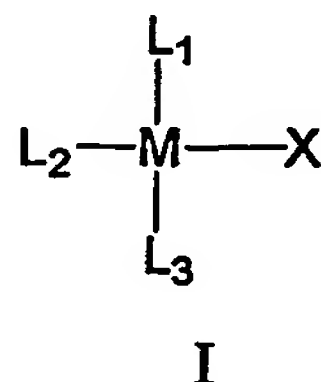
By way of contrast, an atactic polymer is one that has no regular arrangement along the chain.

Another important objective in the field of polymer chemistry has been to develop systems that can control the tacticity of products such as polymethylmethacrylate under industrially relevant process conditions. For example, the higher softening temperature accompanying highly syndiotactic polymethylmethacrylate confers beneficial properties on the resultant materials. Examples include s-PMMA for injection molding, artificial marble pre-mixes, stereocomplexes for preparing membranes and/or gel base materials, and syndiotactic-isotactic block PMMA for forming resist patterns.

To date, a number of systems have been described that can effect syndiotactic control in polymethylmethacrylate. These include organolanthanides [H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake and A. Nakamura, J. Am. Chem. Soc., 1992, 114, 4908; M. Nodono, T. Tokimitsu, S. Tone, T. Makino and A. Yanogase, Macromol. Chem. Phys., 2000, 201, 2282], zirconocenes [A.D. Bolig and E. Y.-X. Chen, J. Am. Chem. Soc., 2001, 123, 7943] aluminium compounds [T. Kitayama, T. Shinozaki, T. Sakamoto, M. Yamamoto and K. Hatada, Makromol. Chem. Suppl., 1989, 15, 167; G.L.N. Péron, R.J. Peace and A.J. Holmes, J. Mater. Chem., 2001, 11, 2915], magnesium compounds [T. Kitayama, T. Shinozaki, E. Masuda, M. Yamamoto and K. Hatada, Polym. Bull., 1988, 20, 565] and enamine initiators [M. Miyamoto and S. Kanetaka, J. Polym. Sci.: Part A: Polym. Chem., 1999, 37, 3671]. Most of these systems are accompanied by one or more limitations: either exceptionally low temperatures (e.g. -78°C or below) are required to obtain high syndiotacticity, and/or the molecular weight control over the resultant product is poor.

The present invention thus seeks to provide a series of discrete, well-defined coordination complexes that are useful as initiators in the polymerisation of alkylacrylate and/or alkylmethacrylate monomers. More specifically, the invention seeks to provide coordination complexes that are capable of influencing and/or controlling the syndiotacticity of the resulting polymer but which alleviate some of the above-mentioned problems associated with prior art complexes.

In a first aspect, the invention provides a complex of formula I



5 wherein

M is Ca, Mg, Ba or Sr;

10 L_1 is selected from R^1O , R^2S , R^3R^4N , R^5R^6P , a substituted or unsubstituted cyclopentadienide, and a substituted or unsubstituted pyrazolyl group, where R^{1-6} are each independently H or hydrocarbyl;

15 L_2 is selected from R^7R^8O , R^7R^8S , $R^7R^8R^9N$, $R^7R^8C=NR^9$, $PR^7R^8R^9$, and a substituted or unsubstituted heterocycle containing one or more O, N or S atoms, where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand;

20 L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2 , wherein L_3 may be the same or different to L_2 ; or L_3 is linked to a further metal centre; or L_1 , L_2 and L_3 are linked to form a tridentate ligand; and

X is an alkyl group, an aryl group, an amide group, an aryloxy or an enolate group of formula $R^{10}R^{11}C=CR^{12}O^-$, wherein R^{10-12} are each independently H or hydrocarbyl;

25 with the proviso that when L_1 and L_2 are $\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}$ and M is magnesium, X is other than Me or tBu .

In a first aspect, the present invention therefore relates to a complex wherein L_1 is a monoanionic ligand, and L_2 and L_3 , if present, are both neutral ligands.

Thus, where L_1 is a substituted or unsubstituted cyclopentadienide, this refers to a monoanionic substituted or unsubstituted cyclopentadiene nucleus which complexes to the metal M. Likewise, where L_1 is a substituted or unsubstituted pyrazolyl group, this refers to a monoanionic pyrazole nucleus. Preferably, the monoanionic pyrazole
5 nucleus complexes to the metal, M, through one of the nitrogen atoms.

As used herein, the term "hydrocarbyl" refers to a group comprising at least C and H that may optionally comprise one or more other suitable substituents. Examples of such substituents may include halo-, alkoxy-, nitro-, an alkyl group, or a cyclic group. In
10 addition to the possibility of the substituents being a cyclic group, a combination of substituents may form a cyclic group. If the hydrocarbyl group comprises more than one C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked via a suitable element or group. Thus, the hydrocarbyl group may contain heteroatoms. Suitable heteroatoms will be apparent to
15 those skilled in the art and include, for instance, sulphur, nitrogen, oxygen, phosphorus and silicon.

Preferably, M is Ca or Mg.

20 In a preferred embodiment, R^1 and R^2 are each independently hydrocarbyl, and R^{3-6} are each independently H or hydrocarbyl.

In a particularly preferred embodiment, R^1 and R^2 are each independently selected from branched or unbranched alkyl, branched or unbranched alkenyl, or aryl, each of which
25 may be substituted or unsubstituted. Suitable substituents include, for example, alkyl, halo-, alkoxy-, nitro-, or a cyclic group.

As used herein, the term "alkyl" refers to a saturated carbon-containing chain which may be straight or branched, and substituted (mono- or poly-) or unsubstituted. Suitable
30 substituents include those which do not have any significant adverse effect on the activity of the complex and may include, for example, halo-, alkoxy-, nitro-, or a cyclic group.

Preferably, the alkyl group is a C₁₋₂₀ alkyl group, more preferably a C₁₋₁₀ alkyl group.

Accordingly, the term "haloalkyl" refers to an alkyl group substituted by at least one halogen, for example, chlorine, bromine, fluorine or iodine.

5

Accordingly, the term "heteroalkyl" refers to an alkyl group containing at least one heteroatom, for example, O, N or S.

As used herein, the term "alkenyl" refers to a C₂₋₂₀ unsaturated carbon-containing chain which may be branched or unbranched, and substituted (mono- or poly-) or unsubstituted. Preferably the alkenyl group is a C₂₋₁₀ alkenyl group.

10

As used herein, the term "aryl" refers to a C₆₋₁₀ aromatic, substituted (mono- or poly-) or unsubstituted. Again, suitable substituents include those which do not have any significant adverse effect on the activity of the complex and may include, for example, alkyl, halo-, alkoxy-, nitro-, or a cyclic group.

15

As used herein, the term "cycloalkyl" refers to a cyclic alkyl group which may be substituted (mono- or poly-) or unsubstituted.

20

As used herein, the term "heterocycle" refers to an aromatic or non-aromatic heterocycle comprising one or more heteroatoms. Preferred heterocycle groups include pyrrole, pyrazole, pyrimidine, pyrazine, pyridine, quinoline, thiophene and furan.

In one preferred embodiment, X is an alkyl group. In an especially preferred embodiment, X is ⁱPr.

25

In another preferred embodiment, X is an amide group. Even more preferably, X is NPrⁱ₂.

30

In another preferred embodiment, X is an enolate group of formula $R^{10}R^{11}C=CR^{12}O-$, wherein R^{10-12} are each independently H or hydrocarbyl. Preferably, R^{10} and R^{11} are H and R^{12} is an aryl group.

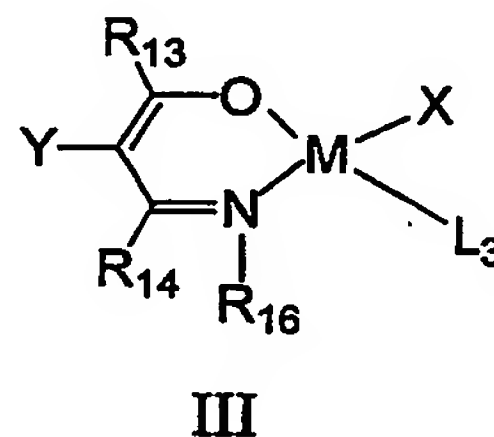
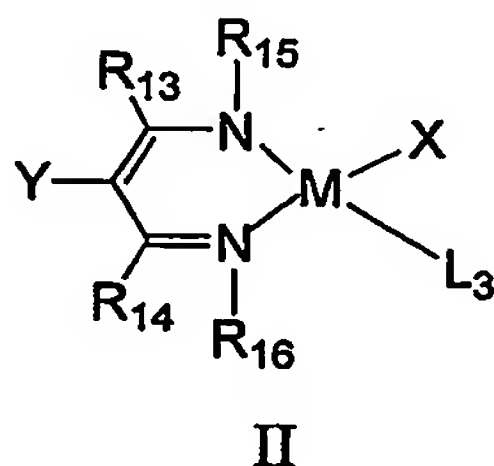
- 5 In one particularly preferred embodiment, X is $-OC(=CH_2)Ar$, wherein $Ar = 2,4,6-$
 $Me_3C_6H_2$.

In one preferred embodiment, L_3 is THF or Et_2O .

- 10 In another preferred embodiment, L_1 and L_2 are linked to form a bidentate ligand selected from derivatives of acetylacetonate, e.g. a beta-diketiminato or a beta-ketoiminato.

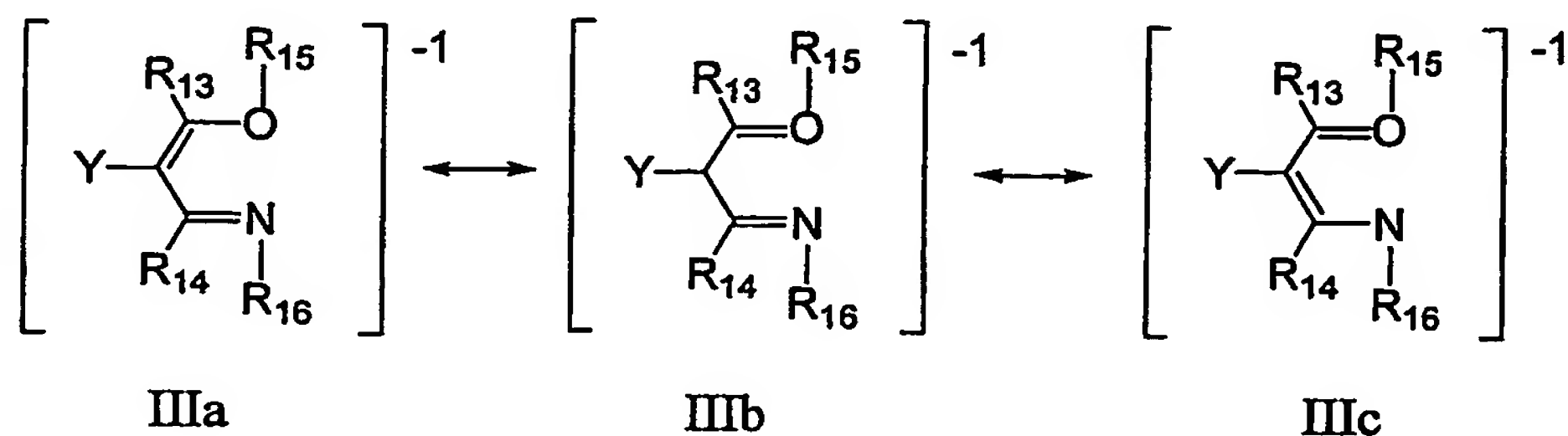
In one preferred embodiment, the complex of the invention is of formula II or III

15

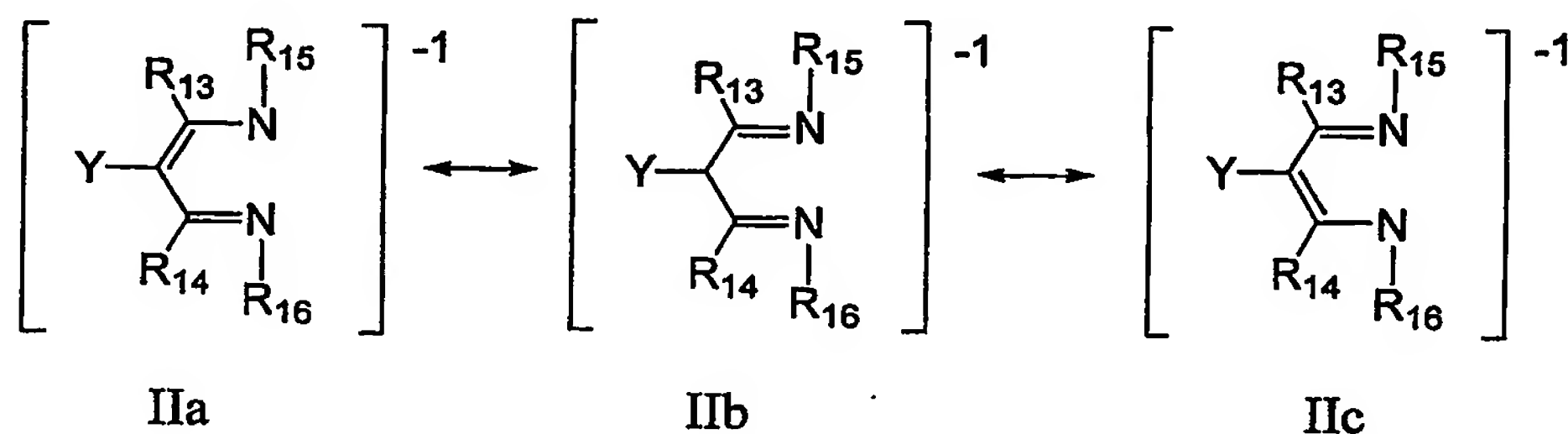


wherein

- 20 Y is H, halogen, NO_2 , hydrocarbyl or CN;
 R^{13-16} are each independently selected from H and hydrocarbyl; or Y and R^{13} are linked to form a hydrocarbyl group; and
 L_3 is as defined above.
- 25 The skilled person will appreciate that ligands of formula III will have an overall charge of -1 and may exist in one or more of the isomeric forms shown below, or mixtures thereof, or a hybrid thereof in which the electrons are delocalised throughout the whole ligand system.



Likewise, the skilled person will appreciate that ligands of formula II will have an overall charge of -1 and may exist in one or more of the isomeric forms shown below, or mixtures thereof, or a hybrid thereof in which the electrons are delocalised throughout the whole ligand system.



10

As used herein, and throughout the accompanying claims and Examples, the shorthand representation of the di-imine isomer IIb, $\{\text{YC}(\text{C}(\text{R}')=\text{N}-\text{R}'')_2\}$, is used for simplicity to represent all of the above isomeric forms of ligand II, in the case where R^{13} and R^{14} are the same (represented as R') and R^{15} and R^{16} are the same (represented as R'').

15

In a more preferred embodiment, where the complex of the invention is of formula II or III, Y is selected from H, halogen, NO_2 , CN, alkyl, aryl, haloalkyl or heteroalkyl;

R^{13-16} are each independently selected from alkyl, aryl, heteroalkyl, haloalkyl, cycloalkyl and a heterocyclic ring containing at least one O, N or S atom; or Y and R^{13} are linked to form an aryl group; and

20

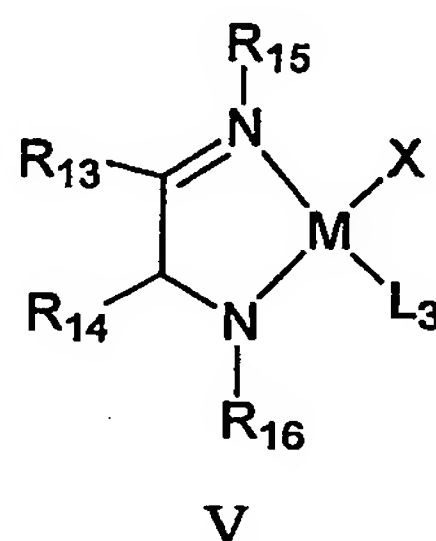
L_3 is selected from $\text{R}^7\text{R}^8\text{O}$, $\text{R}^7\text{R}^8\text{S}$, $\text{R}^7\text{R}^8\text{R}^9\text{N}$, $\text{R}^7\text{C}=\text{NR}^8$, $\text{PR}^7\text{R}^8\text{R}^9$, thiophene and tetrahydrofuran, where R^{7-9} are each independently H or a hydrocarbyl group.

Preferably, where the complex of the invention is of formula II or III, R^{13} and R^{14} are each independently alkyl. In one especially preferred embodiment, R^{13} and R^{14} are the same. More preferably still, R^{13} and R^{14} are both methyl or are both t Bu.

- 5 Preferably, where the complex of the invention is of formula II or III, R^{15} and R^{16} are each substituted aryl groups. In one especially preferred embodiment, R^{15} and R^{16} are the same. More preferably still, R^{15} and R^{16} are both 2,6-diisopropylphenyl.

In another preferred embodiment, the complex of the invention is of formula V

10



- wherein R^{13-16} are as defined above, and where R^{13} and R^{15} are optionally linked to form an aryl group.

15

Preferably, where the complex of the invention is of formula V, R^{13} and R^{14} are the same.

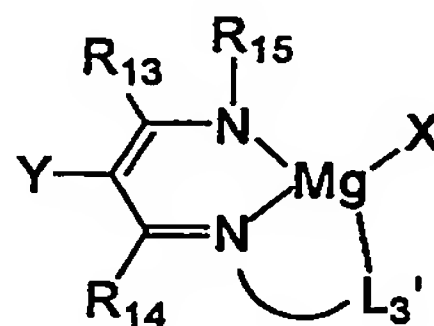
- 20 Preferably, where the complex of the invention is of formula V, R^{15} and R^{16} are the same.

In one preferred embodiment of the invention, L_1 , L_2 and L_3 are linked to form a tridentate ligand.

25

In a particularly preferred embodiment, L_1 , L_2 and L_3 are linked to form a tridentate ligand selected from a beta-diketiminate with a pendant donor group, a Schiff base derivative with a pendant donor arm, and a tris(pyrazolyl)borate ligand.

Even more preferably, the complex of the invention is of formula



VI

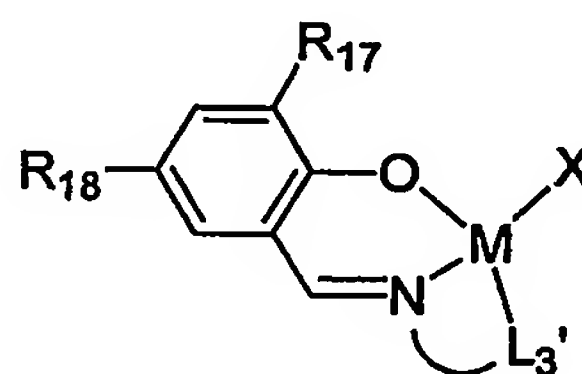
wherein L_3' is defined as for L_3 above, and is linked to the nitrogen of the bidentate ligand via a linker group.

More preferably, the linker group is an aryl group.

In one particularly preferred embodiment, L_3' is an alkoxy group. Even more preferably, the alkoxy group L_3' is attached to an aryl linker group.

In the case where the complex is of formula VI, preferably Y is H, R^{13} and R^{14} are both methyl, R^{15} is aryl (preferably 2,6-diisopropylphenyl) and X is isopropyl.

In an alternative preferred embodiment, the complex of the invention is of formula VII

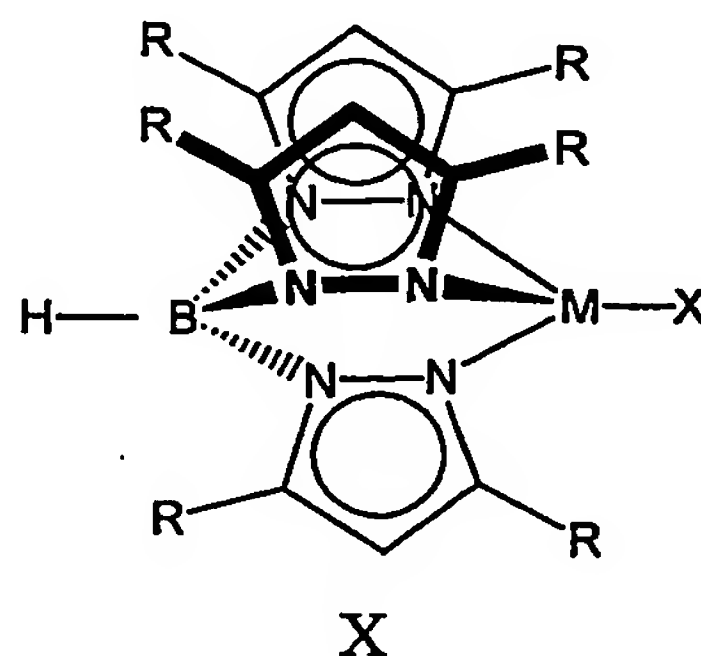


VII

wherein L_3' is defined as for L_3 above, and is linked to the nitrogen of the bidentate ligand via a linker group, and R^{17-18} are as defined for R^{13-16} above.

Preferably, where the complex is of formula VI or VII, the linker group is $(CH_2)_n$ where n is 0-6, an arylene group, or SiR_2 , where R is a hydrocarbyl group.

In another preferred embodiment of the invention, L_1 , L_2 and L_3 are linked to form a tris(pyrazolyl)borate ligand which complexes to metal M as shown below, where each R is independently H or a hydrocarbyl group.



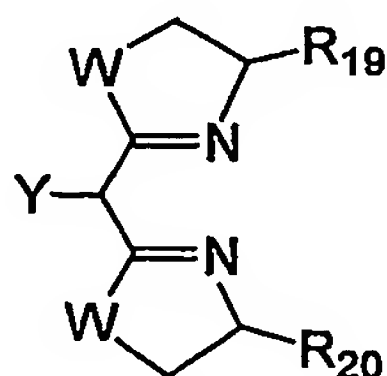
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The tris(pyrazolyl)borate ligand has an overall charge of -1 , i.e., one of the pyrazolyl groups bonds to the metal M as a monoanionic ligand (L_1), whereas the remaining two pyrazolyl groups (L_2 , L_3) complex to metal M as neutral ligands. However, the skilled artisan will appreciate that the electrons in the above tris(pyrazolyl)borate complex are delocalised throughout the whole system.

10

In yet another preferred embodiment of the invention, L_1 and L_2 form a bidentate ligand of formula VIII

15



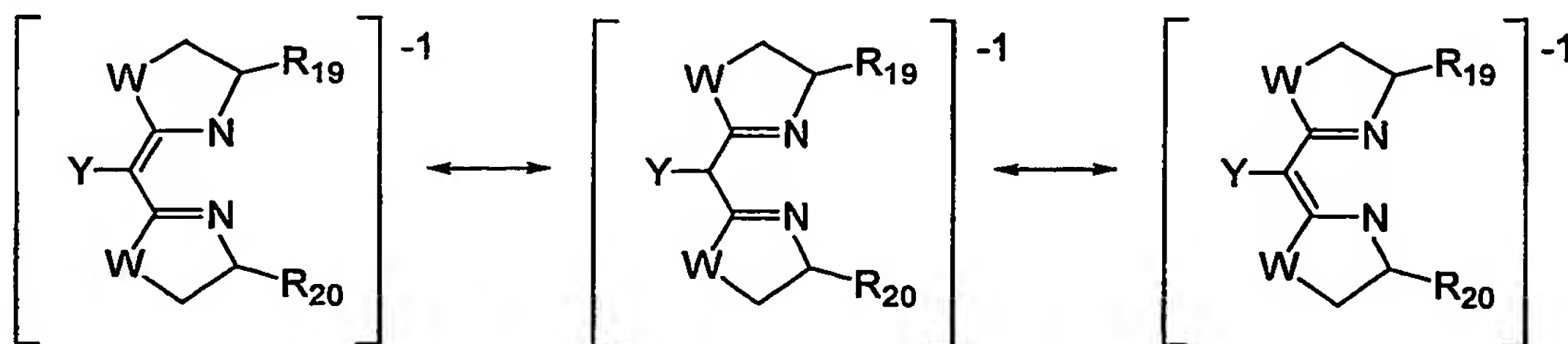
VIII

wherein

20 Y is as defined above;

W is O, NH, NR''' or CH_2 , where R''' is a hydrocarbyl group; and R^{19-20} are as defined for R^{13-16} above.

The skilled person will appreciate that the ligand of formula VIII will have an overall charge of -1 and may exist in one or more of the isomeric forms shown below, or mixtures thereof.



5

In one preferred embodiment, the invention comprises a dimer of a complex as described hereinbefore, or higher nuclearity aggregates.

In an especially preferred embodiment, the complex of the invention is selected from the following:

$\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}Mg^iPr$ [1];

$[\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)]_2$ [2];

$[\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar) \cdot Et_2O]$ [3];

wherein $Ar = 2,4,6-Me_3C_6H_2$;

$\{HC(C^tBu)=N-2,6-iPr_2C_6H_3)_2\}Mg(OC(=CH_2)-2,4,6-Me_3C_6H_2)$ [4];

$\{HC(C(Me)=N-2,6-iPr_2C_6H_3)(C(Me)=N-2-OMeC_6H_4)\}Mg^iPr$ [5];

$\{HB(3,5-Me_2C_3N_2H)_3\}Mg(OC(=CH_2)-2,4,6-Me_3C_6H_2)$ [6];

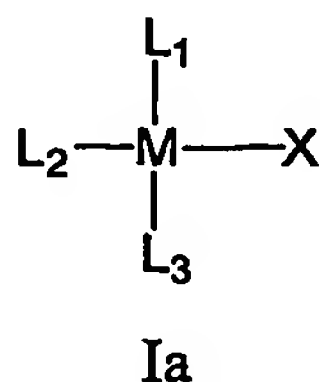
$\{HC(C(Me)=N-2,6-iPr_2C_6H_3)_2\}Ca(OC(=CH_2)-2,4,6-Me_3C_6H_2) \cdot THF$ [7];

$[\{HC(C(Me)=N-2,6-iPr_2C_6H_3)_2\}Ca(OC(=CH_2)-2,4,6-Me_3C_6H_2)]_n$ [8] where $n = 1$ or 2 ;

and

$\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}MgNPr^i_2$ [9].

In a second aspect, the invention relates to the use of a complex of formula Ia as a polymerisation initiator,



25

wherein

M is Ca, Mg, Ba or Sr;

5 L_1 is selected from R^1O , R^2S , R^3R^4N , R^5R^6P , a substituted or unsubstituted cyclopentadienide, and a substituted or unsubstituted pyrazolyl group, where R^{1-6} are each independently H or hydrocarbyl;

10 L_2 is selected from R^7R^8O , R^7R^8S , $R^7R^8R^9N$, $R^7R^8C=NR^9$, $PR^7R^8R^9$, and a substituted or unsubstituted heterocycle containing one or more O, N or S atoms, where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand;

15 L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2 , wherein L_3 may be the same or different to L_2 ; or L_3 is linked to a further metal centre; or L_1 , L_2 and L_3 are linked to form a tridentate ligand; and

X is an alkyl group, an aryl group, an amide group, or an enolate group of formula $R^{10}R^{11}C=CR^{12}O^-$, wherein R^{10-12} are each independently H or hydrocarbyl;

20 with the proviso that when L_1 and L_2 are $\{HC(C(CH_3)=N-2,6-^iPr_2C_6H_3)_2\}$, M is magnesium, X is other than Me or tBu .

Preferably, M is Ca or Mg.

25 The preferred embodiments for the second aspect of the invention are identical to those described hereinabove for the first aspect.

30 In a preferred embodiment, the invention relates to the use of a complex of formula Ia in the polymerisation of acrylate and/or alkylacrylate monomers. In particular, the complexes of the present invention are capable of influencing the tacticity of the resulting polymer. More specifically, the complexes of the invention are capable of inducing a high degree of syndiotacticity in the resulting polymer.

As used herein, the term "acrylate monomer" refers to an acrylate monomer which is optionally substituted by one or more hydrocarbyl groups as defined hereinabove.

Similarly, the term "alkylacrylate monomer" refers to an alkylacrylate monomer which is optionally substituted by one or more hydrocarbyl groups as defined hereinabove.

Preferably, said acrylate and alkylacrylate monomers are substituted by branched acyclic and cyclic hydrocarbons and/or functionalised substituents such as hydroxyalkyl, glycidyl and glycolethers.

10

In one preferred embodiment, the acrylate monomer is an alkylacrylate.

In another preferred embodiment, the alkylacrylate monomer is an alkylmethacrylate.

One preferred embodiment relates to the use of complexes in accordance with the second aspect of the invention as initiators in the preparation of block copolymers. By way of example, said complexes may be used in the preparation of a block copolymer of methyl methacrylate and n-butyl methacrylate. Further details of this aspect of the invention are provided in the accompanying examples section.

20

In a third aspect, the invention provides a process for the polymerisation of acrylate and/or alkylacrylate monomers, said process comprising contacting an initiating amount of a complex of formula Ia as defined above with an acrylate and/or an alkylacrylate monomer in the presence of a suitable solvent.

25

In a preferred embodiment, the invention provides a polymerisation process for preparing a block copolymer, for example, a block copolymer of methyl methacrylate and n-butyl methacrylate.

In a further preferred aspect, the polymerisation takes place in the presence of a chain transfer reagent.

30

Preferably, the chain transfer reagents have an acidic proton in the alpha position to a carbonyl group and are of the formula $Z-CH_2-C(=O)-R''$, wherein R'' is H, alkyl or aryl, and Z is selected from aryl, alkyl, H, amino, alkylamino, acyl, alkoxy (OR), thiol (SR) or heterocycle, where R is a hydrocarbyl group.

5

An example of a chain transfer reagent in which Z is aryl is 2',4',6'-trimethylacetophenone. Examples of chain transfer reagents in which Z is alkylamino include amino methyl ketones and amino ethyl ketones. An example of a chain transfer reagent in which Z is acyl is 2,4-pentanedione, i.e. Z is $C(=O)CH_3$ and R'' is CH_3 .

10

Other suitable chain transfer reagents are known in the literature and will be apparent to the person skilled in the relevant art.

Preferably, the ratio of monomer to the complex in the above process is between 10:1 to $10^6:1$.

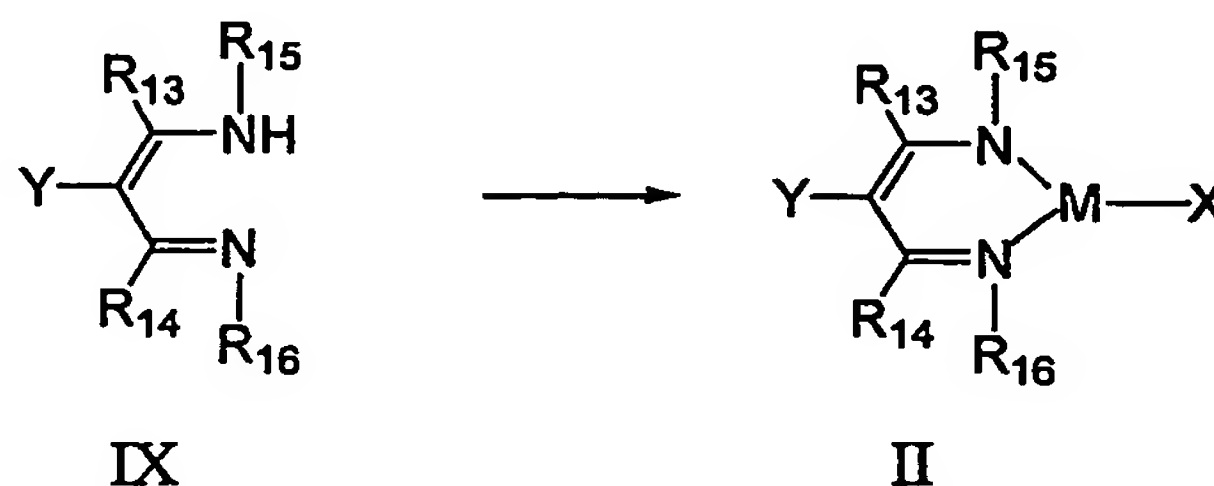
15

A fourth aspect of the invention provides an article prepared by the above-described process.

20 A fifth aspect of the invention provides a composition comprising an acrylate and/or an alkylacrylate monomer and a complex of formula Ia as defined above.

A sixth aspect of the invention provides a composition comprising poly(alkylacrylate) and/or poly(alkylmethacrylate) or co-polymers thereof, and a complex of formula Ia as
25 defined above.

A seventh aspect of the invention relates to a process for preparing a complex of formula II as defined hereinabove, where X is alkyl, said process comprising reacting a compound of formula IX with (a) $nBuLi$, and (b) $XMgCl$



- 5 Alternatively, in an eighth aspect of the invention, the complex of formula II may be prepared by reacting a compound of formula IX with a di(alkyl)magnesium compound, MgX_2 .

In a ninth aspect, the invention provides a process for preparing a complex of formula II,
 10 as defined above, where X is an enolate group of formula $R^{10}R^{11}C=CR^{12}O^-$, said process comprising reacting the product obtained from the above-described seventh and eighth aspects with a compound of formula $HR^{10}R^{11}C-C(O)R^{12}$.

A tenth aspect of the invention provides a method for producing poly(alkylacrylate) or
 15 poly(alkylmethacrylate) having a syndiotacticity of greater than 75%, and preferably greater than 85%, said method comprising contacting the corresponding monomer (alkyl acrylate, or alkylmethacrylate, or mixtures thereof) with a complex of formula Ia as defined above in a suitable solvent.

- 20 Preferably, said method is carried out at a temperature in excess of $-40^\circ C$.

Thus, in one particularly preferred embodiment, the complex of the invention is capable of affording polymethylmethacrylate with greater than 90% syndiotacticity in a highly controlled manner at a temperature in excess of $-40^\circ C$.

25

The invention is further described by way of example and with reference to the following figures wherein:

Figure 1 shows the X-ray crystal structure for the compound $[\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)]_2$.

Figure 2 shows a graph to illustrate the relationship between monomer conversion and M_n as determined by GPC (polydispersities, M_w/M_n , quoted in brackets).

EXAMPLES

Example 1

10 Synthesis of $\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}Mg^iPr$ [1]

$H_2C(C(CH_3)=N-2,6-iPr_2C_6H_3)_2$ (6.880g, 1.64×10^{-2} mol) was dissolved in 50cm³ toluene and lithiated via the addition of 6.7cm³ ⁿBuLi (2.5M in hexane, 1.68×10^{-2} mol). In a separate vessel 8.4cm³ ⁱPrMgCl (2.0M in Et₂O, 1.68×10^{-2} mol) was diluted with 10cm³ toluene and concentrated under reduced pressure to a white viscous liquid.

15 This procedure was repeated in order to remove most of the Et₂O from the Grignard reagent to avoid formation of $[\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}Mg^iPr \cdot Et_2O]$. The white sticky oil thus obtained was suspended in 20cm³ toluene and this mixture was then added dropwise to the solution of $\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}Li$ to afford a pale yellow, cloudy suspension.

20 The reaction was stirred overnight (18hours) at room temperature and then filtered. Volatiles were removed in vacuo and the resultant cream coloured solid was washed with 5cm³ cold (-78°C) n-pentane to afford 7.732g of a slightly off-white powder (1.59×10^{-2} mol, 97.0%).

25 ¹H NMR (C₆D₆): δ 7.10 (m, 6H, *m*-H, *p*-H), 4.92 (s, 1H, HC{C(CH₃)NAr}₂), 3.13 (sept, 4H, ³J_{HH} = 6.9Hz, CHMe₂), 1.67 (s, 6H, HC{C(CH₃)NAr}₂), 1.26 (d, 12H, ³J_{HH} = 6.9Hz, CH(CH₃)₂), 1.14 (d, 12H, ³J_{HH} = 6.9Hz, CH(CH₃)₂), 0.86 (d, 6H, ³J_{HH} = 6.6Hz, MgCH(CH₃)₂), 0.13 (sept, 1H, ³J_{HH} = 6.3Hz, MgCH(CH₃)₂). ¹³C NMR (C₆D₆): δ
30 168.84 (HC{C(CH₃)NAr}₂), 143.63 (C_{ipso}), 141.41 (C_{ortho}), 125.71 (C_{para}), 123.80 (C_{meta}), 94.89 (HC{C(CH₃)NAr}₂), 28.39 (ArCH(CH₃)₂), 24.10 (HC{C(CH₃)NAr}₂),

24.02 (MgCH(CH₃)₂), 23.15 (ArCH(CH₃)₂), 9.22 (MgCH(CH₃)₂). Elemental analysis for C₃₂H₄₈N₂Mg: C 79.24, H 9.97, N 5.78%. Found C 79.31, H 9.94, N 5.68%.

Example 2

5 Synthesis of [$\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)_2$] (Ar = 2,4,6,-
Me₃C₆H₂) [2]

0.8240g $\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}Mg^iPr$ (1.70×10^{-3} mol) was suspended in 20cm³ toluene in a Schlenk tube placed in a solid CO₂ / acetone slush bath at -78°C. A 5cm³ toluene solution of 2',4',6'-trimethylacetophenone (0.2756g, 1.70×10^{-3} mol), also
10 at -78°C, was then added dropwise over 5 minutes to afford a dark orange solution. On warming to ambient temperature the solution becomes increasingly pale yellow.

The reaction was stirred at room temperature for 18 hours. Removal of volatiles from the pale yellow-green solution gave a white solid which was then washed with 10cm³
15 cold heptane (-78°C). A saturated solution was then prepared by stirring the residual white powder in 15cm³ heptane at 60°C for 30 minutes. The solution was filtered and allowed to slowly cool to yield very pale yellow rhomboid crystals of X-ray diffraction quality.

20 A second crop was prepared by reducing the volume of the mother liquor to approximately two-thirds and storing overnight in a freezer at -10°C.

Total yield: 0.673g, 5.58×10^{-4} mol, 65.7%

Example 3

25 Synthesis of [$\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar) \cdot Et_2O$] (Ar = 2,4,6,-
Me₃C₆H₂) [3]

A chilled (-78°C) 10cm³ Et₂O solution of 2',4',6'-trimethylacetophenone (0.4156g, 2.56×10^{-3} mol) was added dropwise over 30 minutes to a 10cm³ Et₂O solution of $\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}Mg^iPr$ (1.2315g, 2.54×10^{-3} mol) in a solid CO₂ /
30 acetone slush bath at -78°C. The reaction was allowed to warm to room temperature to give a pale yellow coloured solution, which was then stirred for a further 18 hours. Volatiles were removed *in vacuo* to give a sticky, cream-coloured solid which was

washed with 5cm³ pentane at -78°C to yield 1.312g of a white powder (1.94 x 10⁻³mol, 76.3%).

Example 4

5 Typical polymerisation procedure for [$\{HC(C(CH_3)=N-2,6-^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)_2$] [2]

0.0084g [$\{HC(C(CH_3)=N-2,6-^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)_2$] (1.39 x 10⁻⁵mol) was weighed out into a glass vial and dissolved in 5cm³ toluene to afford a pale yellow solution. The solution was cooled to -30°C. Methyl methacrylate (0.4183g, 4.18 x 10⁻³mol, 300 equivalents) was then weighed out and cooled to -30°C and added to the initiator solution. The mixture was stirred for 10 minutes, followed by termination of the polymerisation by addition of 25μl MeOH.

GPC analysis was performed on a small aliquot, which was removed and dried in vacuo. The remainder of the solution was added to a large excess (ca. 150cm³) MeOH, and the precipitate was collected and dried. ¹H NMR analysis (CDCl₃) gave 92% rr, 8%rm, (mm triad undetected).

Example 5

20 Typical polymerisation procedure for [$\{HC(C(CH_3)=N-2,6-^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar) \cdot Et_2O$] [3]

An identical method to that described above was employed. No significant differences in the behaviour of the polymerisation using the etherate initiator were observed.

25 Example 6

Typical polymerisation procedure for [$\{HC(C(CH_3)=N-2,6-^iPr_2C_6H_3)_2\}Mg^iPr$] [1]

An identical method to the procedure outlined for [$\{HC(C(CH_3)=N-2,6-^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)_2$] was used. Immediately upon addition of methyl methacrylate to the initiator solution a bright yellow colouration was observed, which quickly became pale yellow. This colour persisted through the remainder of the reaction, disappearing upon addition of MeOH.

Example 7Investigation into the relationship between conversion and molecular weight

- Using a similar method to that described above, 0.0080g [$\{HC(C(CH_3)=N-2,6-^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)_2$] ($1.33 \times 10^{-5}mol$) was dissolved in 6cm³ CDCl₃. To this solution at -30°C was added neat methyl methacrylate (0.5317g, $5.31 \times 10^{-3}mol$, 400 equivalents). The reaction was stirred at -30°C and at set time periods (120, 240, 360 and 480 seconds), 0.35cm³ aliquots were removed and immediately terminated by addition to 20μl MeOH.
- 10 Monomer conversion was calculated by diluting the samples with a further 0.35cm³ CDCl₃ and integrating the ¹H NMR resonances of the OCH₃ signals of the monomer (δ3.71) versus the polymer (δ3.56). Volatiles were then removed in vacuo and the residue was dissolved in non-deuterated CHCl₃. Analysis of this solution by gel permeation chromatography afforded a correlation of M_n versus conversion (see Figure 15 2).

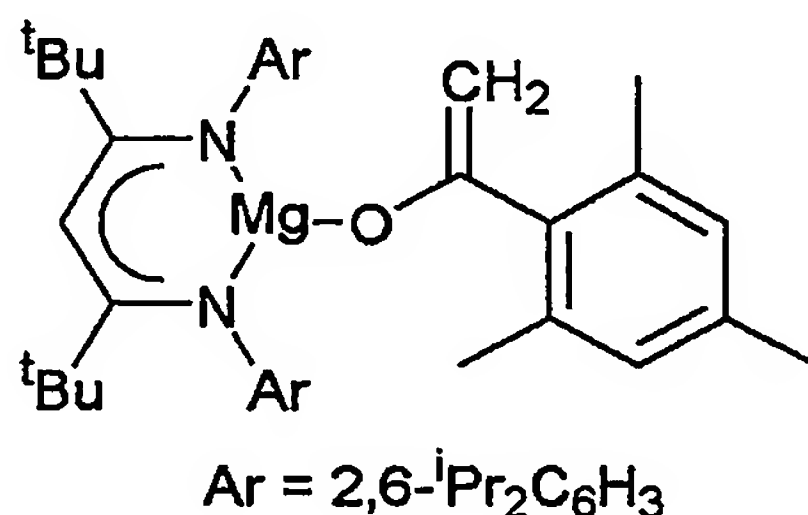
Example 8Block copolymerisation of n-butylmethacrylate (BMA) and methylmethacrylate (MMA)

- 20 0.0106g [$\{HC(C(CH_3)=N-2,6-^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)_2$] ($1.76 \times 10^{-5}mol$) was dissolved in 3cm³ CDCl₃ at -30°C. To this stirring solution was added 0.2526g BMA ($1.78 \times 10^{-5}mol$, 101 equivalents). After 10 minutes a 300μl aliquot was removed and terminated by addition to 10μl MeOH. The polymerisation was allowed to stir for a further 60 seconds and then 0.1756g MMA ($1.75 \times 10^{-5}mol$, 100 equivalents) was added. The reaction was stirred for a further 10 minutes and terminated by addition of 25μl MeOH. ¹H NMR on the aliquot revealed that before the addition of the second monomer the BMA had been totally consumed.

- GPC on the aliquot before addition of the MMA showed a single, monodisperse peak (M_n calc = 14,400, M_n obs = 13,800, M_w/M_n = 1.12). GPC on the block copolymer demonstrated M_n increased upon the incorporation of the MMA (M_n calc = 24,400, M_n obs = 22,800, M_w/M_n = 1.50).

Example 9The use of 2',4',6'-trimethylacetophenone as a chain transfer agent

To a 3cm³ CDCl₃ solution of [$\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)_2$] (0.0130g, 2.16×10^{-5} mol) at -30°C was added 17.9μl 2',4',6'-trimethylacetophenone (1.08 x 10⁻⁴mol, 5.0 equivalents) to afford a bright yellow solution. 0.8675g MMA (8.66 x 10⁻⁵mol, 402 equivalents) was then added. After 30 minutes the reaction was terminated by the addition of 25μl MeOH. GPC Mn calc (assuming maximum chain transfer) = 6,700; Mn obs = 7,200, Mw/Mn = 2.83).

10 Example 10Synthesis of $\{HC(C^tBu)=N-2,6-iPr_2C_6H_3)_2\}Mg(OC(=CH_2)-2,4,6-Me_3C_6H_2)$ [4]

15 0.8902g H₂C(C(^tBu)=N-2,6-*i*Pr₂C₆H₃)₂ (1.77×10^{-3} mol) was dissolved in 10cm³ toluene and then chilled to -78°C. Bu₂Mg (1.86cm³, 1.0M solution in heptane, 1.86×10^{-3} mol, 1.05 equivalents) was added dropwise over 5 minutes, and upon removal from the cold bath a light yellow solution developed. The reaction was allowed to reach room temperature and then stirred for 2 hours at 60°C. The reaction vessel was then allowed
20 to cool to room temperature before 0.30cm³ 2',4',6'-trimethylacetophenone (1.81×10^{-3} mol, 1.02 equivalents) was added. The mixture was then warmed back to 60°C and stirred for 90 mins. The volatile components were then removed *in vacuo* to give a yellow oily solid which was washed with pentane (5cm³) at -78°C.

25 ¹H NMR (C₆D₆): δ 7.12-6.97 (m, 6H, N-2,6-*i*Pr₂C₆H₃), 6.72 (s, 2H, 2,4,6-Me₃C₆H₂), 5.40 (s, 1H, HC{C(^tBu)=NAr}₂), 3.77 (d, ²J_{HH} = 0.9Hz, 1H, OC(=CHH)Ar'), 3.66 (d, ²J_{HH} = 1.0Hz, 1H, OC(=CHH)Ar'), 3.22 (sept, 4H, ³J_{HH} = 6.9Hz, CHMeMe) 2.17 (s,

6H, mesityl *o*-CH₃), 1.98 (s, 3H, mesityl *p*-CH₃), 1.22 (d, 12H, ³J_{HH} = 6.8Hz, CHMeMe), 1.21 (d, 12H, ³J_{HH} = 6.98Hz, CHMeMe), 1.14 (s, 18H, HC{C(CMe₃)=NAr}₂).

5 Example 11

Use of {HC(C(^tBu)=N-2,6-ⁱPr₂C₆H₃)₂}Mg(OC(=CH₂)-2,4,6-Me₃C₆H₂) [4] as an MMA polymerisation initiator

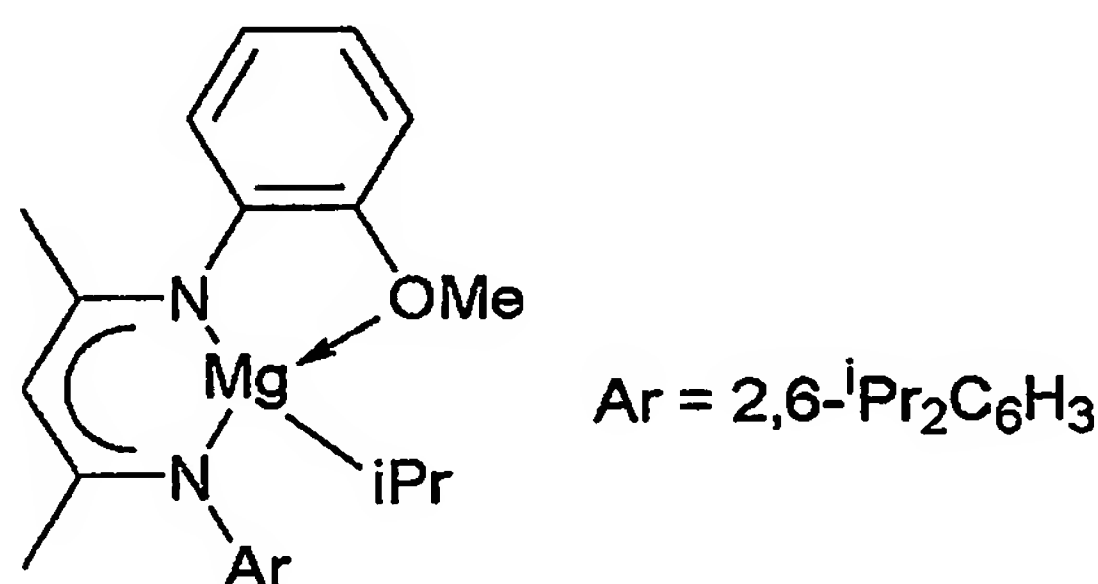
A similar method to that described for the synthesis of {HC(C(Me)=N-2,6-ⁱPr₂C₆H₃)₂}Mg(OC(=CH₂)-2,4,6-Me₃C₆H₂) was used. The polymerisation using
 10 {HC(C(^tBu)=N-2,6-ⁱPr₂C₆H₃)₂}Mg(OC(=CH₂)-2,4,6-Me₃C₆H₂) is slower, however. Thus, for 200 equivalents MMA a reaction time of 120 minutes is required at -30°C to afford x% conversion (c.f. < 5 minutes for {HC(C(Me)=N-2,6-ⁱPr₂C₆H₃)₂}Mg(OC(=CH₂)-2,4,6-Me₃C₆H₂).

M_n = 17,100 (M_n calc = 20,000); M_w/M_n = 1.04.

15 Syndiotactic content (% rr triad) = 90%

Example 12

Synthesis of {HC(C(Me)=N-2,6-ⁱPr₂C₆H₃)(C(Me)=N-2-OMeC₆H₄)}MgⁱPr [5]



20

ⁿButyl lithium (2.70 mL, 2.5M in hexanes, 6.75 x 10⁻³mol) was added slowly to a stirred solution of {H₂C(C(Me)=N-2,6-ⁱPr₂C₆H₃)(C(Me)=N-2-OMeC₆H₄)} (2.46 g, 6.75 x 10⁻³mol) in 25 mL toluene at 0°C. The solution was stirred for 24 hours before
 25 addition of ⁱPrMgCl (3.37cm³, 2.0M in Et₂O, 6.74 x 10⁻³mol) at 0°C. The solution was then stirred for a further 18 hours at ambient temperature. Concentration of the solution under reduced pressure afforded an orange solid (2.1 g, 4.98 x 10⁻³mol, 73.9 %).

^1H NMR (C_6D_6): δ 6.87, 6.79, 6.48 (m, 7H, ArH), 4.90 (s, 1H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 3.32 (s, 3H, ArOCH_3), 3.20 (sept, 1H, $^3J_{\text{HH}} = 6.86$ Hz, ArCHMe_2), 1.92 (s, 3H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 1.68 (s, 3H, $\text{HC}\{\text{C}(\text{CH}_3)\text{NAr}\}_2$), 1.24 (d, 6H, $^3J_{\text{HH}} = 6.44$ Hz, $\text{ArCH}(\text{CH}_3)_2$), 1.23 (d, 6H, $^3J_{\text{HH}} = 7.86$ Hz, $\text{MgCH}(\text{CH}_3)_2$), 1.16 (d, 6H, $^3J_{\text{HH}} = 6.83$ Hz, $\text{ArCH}(\text{CH}_3)_2$), 0.07 (sept, 1H, $^3J_{\text{HH}} = 7.83$ Hz, MgCHMe_2).

Example 13

Use of $\{\text{HC}(\text{C}(\text{Me})=\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)(\text{C}(\text{Me})=\text{N}-2\text{-OMeC}_6\text{H}_4)\}\text{Mg}^i\text{Pr}$ [5] as an MMA polymerisation initiator

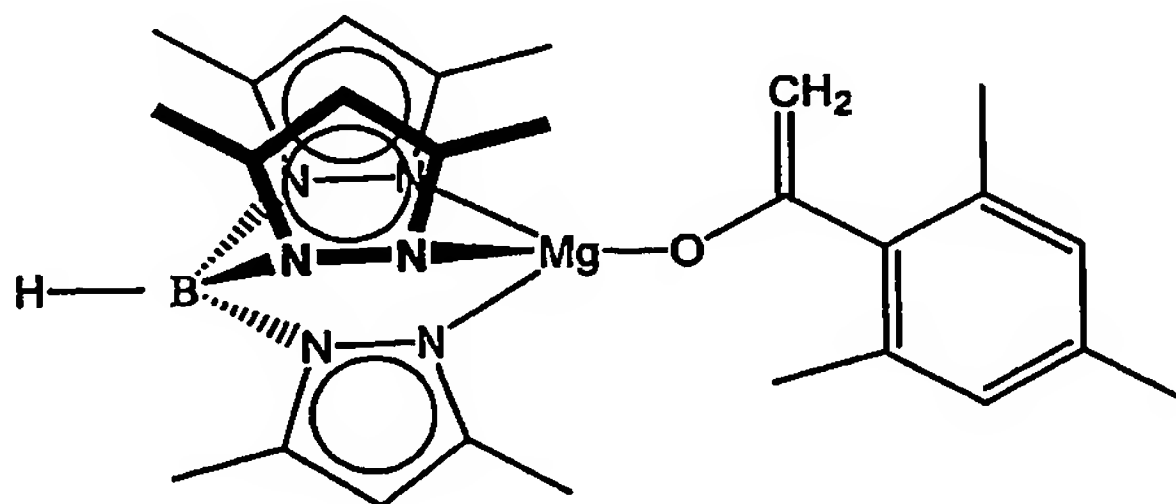
10 In toluene at -30°C , 200 equivalents MMA attains a conversion of 74% after 120 seconds.

$M_n = 24,677$ (M_n calc = 14,800), $M_w/M_n = 1.20$

Syndiotactic content (% rr triad) = 85%

15 Example 14

Synthesis of $\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{N}_2\text{H})_3\}\text{Mg}(\text{OC}(=\text{CH}_2)\text{-}2,4,6\text{-Me}_3\text{C}_6\text{H}_2)$ [6]



20 Potassium tris(3,5-dimethylpyrazolyl)borate (0.8945g, 2.66×10^{-3} mol) was suspended in 20cm^3 THF. 1.36cm^3 $^i\text{PrMgCl}$ (2.0M in Et_2O , 2.72×10^{-3} mol, 1.02 equivalents) was added via syringe at room temperature and the resultant white suspension was stirred for 6 hrs at 60°C . The reaction mixture was then allowed to cool to room temperature before a 10cm^3 THF solution of 0.4401g 2',4',6'-trimethylacetophenone (2.71×10^{-3} mol, 1.02 equivalents) was added dropwise over 2 minutes. The reaction was stirred at

25 room temperature for 16 hours, filtered and concentrated to a white solid. This was washed with 5cm^3 cold pentane (-78°C) and dried in vacuo to afford a free flowing white powder.

^1H NMR (CDCl_3): δ 6.83 (s, 2H, 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$), 4.19 (d, $^2J_{\text{HH}} = 0.8\text{Hz}$, 1H, $\text{OC}(=\text{CHH})\text{Ar}'$), 3.70 (d, $^2J_{\text{HH}} = 0.9\text{Hz}$, 1H, $\text{OC}(=\text{CHH})\text{Ar}'$), 3.70 (s, br, BH), 2.47 (s, 6H, mesityl *o*- CH_3), 2.35 (s, 9H, $\text{HB}\{\text{C}_3\text{N}_2\text{H}(\text{CH}_3)_2\}$), 2.26 (s, 3H, mesityl *p*- CH_3), 2.22 (s, 9H, $\text{HB}\{\text{C}_3\text{N}_2\text{H}(\text{CH}_3)_2\}$)

5

Example 15

Use of $\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{N}_2\text{H})_3\}\text{Mg}(\text{OC}(=\text{CH}_2)\text{-}2,4,6\text{-Me}_3\text{C}_6\text{H}_2)$ [6] as an MMA polymerisation initiator

0.0080g $\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{N}_2\text{H})_3\}\text{Mg}(\text{OC}(=\text{CH}_2)\text{-}2,4,6\text{-Me}_3\text{C}_6\text{H}_2)$ ($1.66 \times 10^{-5}\text{mol}$) was dissolved in 2 cm^3 toluene and chilled to -30°C . To this solution was added a 1 cm^3 toluene solution of MMA (0.3360g, $3.36 \times 10^{-3}\text{mol}$, 202 equivalents) and the reaction was stirred for 2 hours at -30°C .

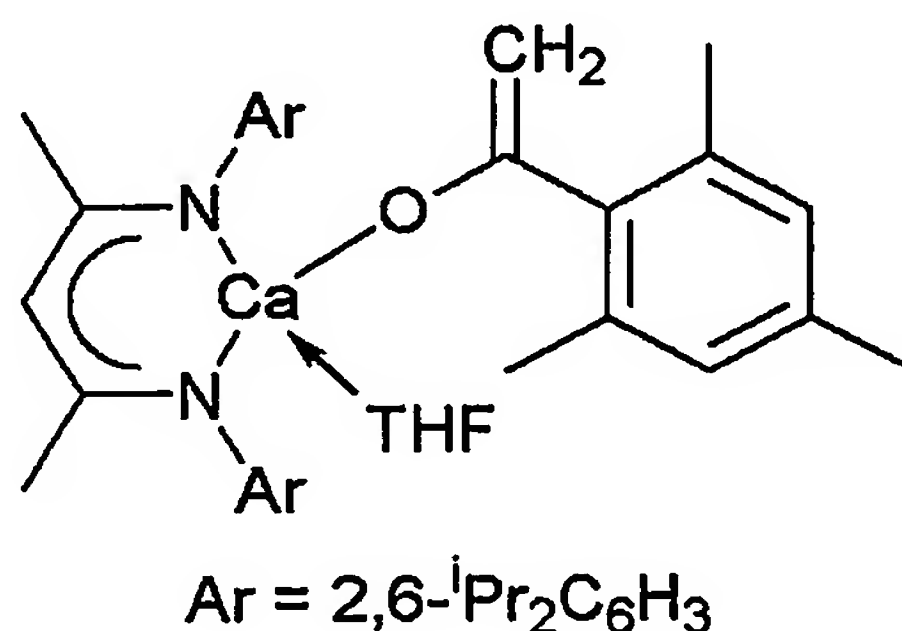
$M_n = 31,100$ (calc = 20,200), $M_w/M_n = 1.52$

Triad analysis (by ^1H NMR): 14.5% mm : 20.5% rm : 65.0% rr

15

Example 16

Synthesis of $\{\text{HC}(\text{C}(\text{Me})=\text{N-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\}\text{Ca}(\text{OC}(=\text{CH}_2)\text{-}2,4,6\text{-Me}_3\text{C}_6\text{H}_2) \cdot \text{THF}$ [7]



20

$\{\text{HC}(\text{C}(\text{Me})=\text{N-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\}\text{CaNTMS}_2 \cdot \text{THF}$ (0.0089g, $1.29 \times 10^{-5}\text{mol}$) and 2',4',6'-trimethylacetophenone (0.0021g, $1.29 \times 10^{-5}\text{mol}$) were mixed together in THF-d_8 . ^1H NMR spectroscopy confirms the formation of $\{\text{HC}(\text{C}(\text{Me})=\text{N-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\}\text{Ca}(\text{OC}(=\text{CH}_2)\text{-}2,4,6\text{-Me}_3\text{C}_6\text{H}_2) \cdot \text{THF}$ and HNTMS_2 .

25

^1H NMR (THF- d_8): δ 7.06 (m, br, 6H, N-2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$), 6.60 (s, br, 2H, 2,4,6-Me- $_3\text{C}_6\text{H}_2$), 4.85 (s, br, 1H, $\text{HC}\{\text{C}(\text{tBu})=\text{NAr}\}_2$), 4.73 (s, br, 1H, $\text{OC}(=\text{CHH})\text{Ar}'$), 3.41 (s, br, 1H, $\text{OC}(=\text{CHH})\text{Ar}'$), 3.17 (m, br, 4H, CHMeMe), 2.16 (s, br, 6H, mesityl *o*- CH_3), 1.70 (s, br, 6H, $\text{HC}\{\text{C}(\text{Me})=\text{NAr}\}_2$), 1.60 (s, 3H, mesityl *p*- CH_3), 1.11 (m, br, 24H, $^3\text{J}_{\text{HH}} = 6.8\text{Hz}$, CHMe_2).

Example 17

Synthesis of $[\{\text{HC}(\text{C}(\text{Me})=\text{N}-2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)_2\}\text{Ca}(\text{OC}(=\text{CH}_2)-2,4,6-\text{Me}_3\text{C}_6\text{H}_2)]_n$ [8]

Mixing $\{\text{HC}(\text{C}(\text{Me})=\text{N}-2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)_2\}\text{CaNTMS}_2\cdot\text{THF}$ (0.0219g, $3.17 \times 10^{-5}\text{mol}$) and 2',4',6'-trimethylacetophenone (0.0051g, $3.17 \times 10^{-5}\text{mol}$) in benzene- d_6 affords $[\{\text{HC}(\text{C}(\text{Me})=\text{N}-2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)_2\}\text{Ca}(\text{OC}(=\text{CH}_2)-2,4,6-\text{Me}_3\text{C}_6\text{H}_2)]_n$.

^1H NMR (C_6D_6): δ 7.19-7.06 (m, 6H, N-2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$), 6.65 (s, 2H, 2,4,6-Me $_3\text{C}_6\text{H}_2$), 4.62 (s, 1H, $\text{HC}\{\text{C}(\text{tBu})=\text{NAr}\}_2$), 4.18 (s, br, 1H, $\text{OC}(=\text{CHH})\text{Ar}'$), 3.83 (s, br, 1H, $\text{OC}(=\text{CHH})\text{Ar}'$), 3.12, 3.04 (sept, 4H, $^3\text{J}_{\text{HH}} = 6.9\text{Hz}$, CHMeMe), 2.10 (s, 6H, mesityl *o*- CH_3), 1.98 (s, 3H, mesityl *p*- CH_3), 1.53 (s, 6H, $\text{HC}\{\text{C}(\text{Me})=\text{NAr}\}_2$), 1.16 - 1.08 (m, br, 24H, CHMeMe)

Example 18

Use of $[\{\text{HC}(\text{C}(\text{Me})=\text{N}-2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)_2\}\text{Ca}(\text{OC}(=\text{CH}_2)-2,4,6-\text{Me}_3\text{C}_6\text{H}_2)]_n$ [8] as an MMA polymerisation initiator

At -30°C a 0.5cm^3 toluene solution of 2',4',6'-trimethylacetophenone (0.0022g, $1.36 \times 10^{-5}\text{mol}$) was added to a 2cm^3 toluene solution of $\{\text{HC}(\text{C}(\text{Me})=\text{N}-2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)_2\}\text{CaNTMS}_2\cdot\text{THF}$ (0.0091g, $1.32 \times 10^{-5}\text{mol}$). After stirring for 1 minute, MMA (0.2657g, $2.65 \times 10^{-3}\text{mol}$, 201 equivalents in 1cm^3 toluene) was added dropwise over 20s.

The polymerisation was stirred at -30°C for 5 minutes, then terminated with MeOH (25 μl).

^1H NMR confirms that the PMMA is isotactic-biased: triad contents = 70.8% mm :

22.7% mr : 6.5% rr

$M_n = 41,850$, $M_w/M_n = 6.09$

Example 19Synthesis of $\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}MgNPr^i_2$ [9]

A stirred toluene solution of 2.0×10^{-3} mol $[(BDD)Mg^{n/s}Bu]$ (formed in situ from the reaction of Bu_2Mg with $H_2C(C(CH_3)=N-2,6-iPr_2C_6H_3)_2$) was cooled to $-30^\circ C$ and
5 treated dropwise with iPr_2NH (290 μl , 2.1×10^{-3} mol). The resulting solution was allowed to warm to ambient temperature, and then stirred at $60^\circ C$ for 15 minutes. Volatiles were then removed in vacuo and the residue then extracted into pentane (35 ml). Upon standing at $-30^\circ C$ 0.67g crystals formed (62%).

10 1H NMR (C_6D_6): δ 7.12 (m, 6H, *m-H*, *p-H*), 4.84 (s, 1H, $HC\{C(CH_3)NAr\}_2$), 3.23 (sept, 4H, $^3J_{HH} = 6.7Hz$, $CHMe_2$), 3.07 (sept, 2H, $^3J_{HH} = 6.1Hz$, $NCH(CH_3)_2$), 1.66 (s, 6H, $HC\{C(CH_3)NAr\}_2$), 1.34 (d, 12H, $^3J_{HH} = 6.9Hz$, $CH(CH_3)_2$), 1.17 (d, 12H, $^3J_{HH} = 6.9Hz$, $CH(CH_3)_2$), 0.87 (d, 12H, $^3J_{HH} = 6.1Hz$, $NCH(CH_3)_2$).

15 Example 20Use of $\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}MgNPr^i_2$ [9] as an MMA polymerisation initiator

In toluene at $-30^\circ C$, 200 equivalents MMA were mixed with $\{HC(C(CH_3)=N-2,6-iPr_2C_6H_3)_2\}MgNPr^i_2$. The polymerisation was terminated after 90seconds with MeOH.
20 A conversion of 94% was measured by 1H NMR spectroscopy.
 $M_n = 19,550$ (M_n calc = 18,800); $M_w/M_n = 1.05$.
Syndiotactic content (% rr triad) >90%

Various modifications and variations of the described methods of the invention will be
25 apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims.